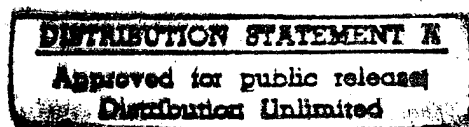


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# Industrial Process Profiles for Environmental Use: Chapter 13 Plasticizers Industry

Radian Corp, Austin, TX



DEPARTMENT OF DEFENSE  
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Environmental Protection Technology Series

INDUSTRIAL PROCESS PROFILES FOR  
ENVIRONMENTAL USE: Chapter 13  
Plasticizers Industry



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This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

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16. ABSTRACT The catalog of Industrial Process Profiles for Environmental Use was developed as an aid in defining the environmental impacts of industrial activity in the United States. Entries for each industry are in consistent format and form separate chapters of the study. The Plasticizer Industry includes manufacturers who produce primary synthetic organic plasticizers. Manufacturers who refine or otherwise upgrade natural plasticizers such as mineral oil or castor oil are not included. Plasticizers are materials which are added to organic polymers to facilitate processing, to modify the properties of the product, or both. In many cases, the distinction between plasticizers and other additives, such as extender oils, flame retardants, processing aids and lubricants are often blurred. Three process flow sheets and three process descriptions have been prepared to characterize the industry. Within each process description available data have been presented on input materials, operating parameters, utility requirements, and waste streams. Data related to the subject matter, including company and product data, are included as appendices.		
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INDUSTRIAL PROCESS PROFILES

ENVIRONMENTAL USE

CHAPTER 13

PLASTICIZERS INDUSTRY

by

Carol May Thompson  
Radian Corporation  
Austin, Texas 78766

Contract No. 68-02-1319

Project Officer  
Alfred B. Craig  
Metals and Inorganic Chemicals Branch  
Industrial Environmental Research Laboratory  
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY  
OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
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## CHAPTER 13

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## SYNTHETIC PLASTICIZER INDUSTRY

### INDUSTRY DESCRIPTION

The plasticizer industry includes manufacturers who produce primary synthetic organic plasticizers. Manufacturers who refine or otherwise upgrade natural plasticizers such as mineral oil or castor oil are not included. Plasticizers are materials which are added to organic polymers to facilitate processing, to modify the properties of the product, or both. In some cases the plasticizer serves primarily as a processing aid, facilitating the fabrication of the polymer into its final product but performing no function thereafter. In other cases the plasticizer determines the physical properties of the end product and is a critically important, functional component of the composite for the life of the end product. In general, workability, flexibility, extensibility and resilience are imparted to a polymer system by a plasticizer. Distinctions among plasticizers, extender oils, flame retardants, processing aids and lubricants are often blurred.

Amounts of plasticizer added vary from a few percent to amounts comparable to the amount of organic polymer in the finished product. Plasticizers compatible with one polymer may not be compatible with another. Primary plasticizers have a high degree of compatibility with the polymer at the projected use level. A second or extender plasticizer can be used safely only with substantial amounts of primary plasticizer for the polymer system to maintain satisfactory compatibility. Extenders are used to reduce costs. The plasticizer industry uses raw materials produced by the industrial organic chemicals industry (Chapter 6) and produces products which are used as raw materials by the plastics and resins industry (Chapter 10). There are more than 600 plasticizers commercially available but only about 150 of these have industrial significance. The bulk of plasticizers used currently in the United States is employed in the formulation of flexible vinyl plastics.

The major categories of synthetic plasticizers are carboxylic acid esters, phosphoric acid esters, linear polyesters and epoxidized esters. Most synthetic plasticizers are derived from some form of esterification.

Seventeen manufacturing facilities owned by 13 companies accounted for 93 percent of the 1974 plasticizers production capacity (980 Gg/yr). Numerous small firms are engaged in the production of plasticizers for specialty applications.

According to the Standard Industrial Classification System, the plasticizer industry is included in the group of industries which produces a wide range of synthetic organic chemicals. Since industry statistics for this group of manufacturers are combined, no information was found describing the approximate number of workers employed in the production of plasticizers.

The United States International Trade Commission (formerly U. S. Tariff Commission) reported total production of primary plasticizers in 1974 to be 858 Gg (1.89 billion pounds). Table 1 lists the production figures reported by the Tariff Commission. As indicated in Table 1 well

over half of U. S. synthetic plasticizer production is of phthalate esters. Production included 70 Gg of epoxidized esters (epoxidized soya oils and octylepoxytallates): 16 Gg of esters of natural fatty acids such as oleic, sebacic and stearic acids; and 56 Gg of other acrylic plasticizers. It is possible that some of the production by some of these categories does not refer to the synthetic plasticizer industry as it has been defined here.

Table 1. 1974 PRODUCTION OF PRIMARY PLASTICIZERS BY GROUPS

Plasticizer Type	Production (Gg)
Phthalic acid esters	548
Trimellitic acid esters	12
Other cyclic (non-phosphate plasticizers)	38
Adipic acid esters	29
Epoxidized esters	70
Esters of oleic, stearic, and sebacic acids	16
Other acyclic (non-phosphate) plasticizers	61
Cyclic phosphates	43
Acyclic phosphates	13
Complex linear polyesters	29
	—
TOTAL	858

Source: United States International Trade Commission. Synthetic Organic Chemicals, United States Production and Sales of Plasticizers. 1974, Preliminary, December 1975.

Manufacturing plants, with several minor exceptions, are located east of the Mississippi River. The plants are evenly distributed north to south with some concentrations along the eastern seaboard. Appendix C gives plant site locations.

About 80 percent of all plasticizers are consumed in poly(vinyl chloride) (PVC) formulations; therefore, trends in the synthetic plasticizer industry generally follow those of flexible poly(vinyl chloride) production. Table 2 lists total U.S. production of plasticizers as reported

by the International Trade Commission.

Table 2. TOTAL U.S. PLASTICIZER PRODUCTION FOR 1965-1974

Year	Production (Gg/yr)
1965	587
1966	548
1967	573
1968	604
1969	627
1970	606
1971	678
1972	775
1973	850
1974	858

Source: U.S. Tariff Commission Synthetic Organic Chemicals, United States Production and Sales. Plasticizers. 1965 TC Publication 206; 1966 TC Publication 248; 1967 Preliminary; 1968 Preliminary; 1969 Preliminary; 1970 TC Publication 479; 1971 TC Publication 614; 1972 TC Publication 681. United States International Trade Commission, Synthetic Organic Chemicals, United States Production and Sales. Plasticizers 1973 ITC Publication 728; 1974 Preliminary.

Production of poly(vinyl chloride) resins and products dropped approximately 25 percent from 1974 to 1975. Assuming plasticizer production followed the same trend, 1975 production would be estimated at about 645 Gg. This drop in production was brought on by greatly decreased demand from the automotive and housing industries. The only other annual decrease in plasticizer production in the past 10 years is correlated with the 1969-70 economic slowdown. Economic recovery is expected to return the growth rate for plasticizers to the 5-10 percent per year range.

Despite these optimistic predictions uncertainties exist in the long-range future of poly(vinyl chloride) based products and therefore in the future demand for synthetic plasticizers. These uncertainties arise from solid waste disposal problems and toxicity problems. Solid waste disposal problems include the nondegradability problems associated with plastics in

general when the landfill method of disposal is used. In addition, incineration of unplasticized poly(vinyl chloride) resin yields 0.6 kg of HCl, a corrosive and toxic gas, per kg of resin. (In a typical flexible [plasticized] product containing approximately 35 percent plasticizer the amount of HCl emitted would be proportionately reduced.) At low combustion temperatures the presence of chlorine retards combustion. Environmentally acceptable incineration of large amounts of poly(vinyl chloride) requires the use of specially designed incinerators to promote combustion, resist corrosion, and prevent hazardous emissions.

Toxicity questions associated with poly(vinyl chloride) revolve around the discovery of previously unknown toxic properties of vinyl chloride monomer in the early seventies. These discoveries resulted in stringent emission standards which have raised some doubts about the future of vinyl chloride. The toxicity of phthalate esters has been a matter of concern. However, possible effects on humans have not been clearly demonstrated. So far, concerns related to the environment and safety have not influenced the plasticizer market nearly so much as have economic factors.

Short-term estimates of raw materials supplies (phthalic anhydride, branched alcohols and linear alcohols) indicate adequate supplies in most cases for the next two to four years. The long-term outlook for feedstock supply and price (which impact product prices) is tied to the political and economic complexities associated with the increasing reliance of the United States on imported petroleum.

The plasticizer industry, along with the entire petrochemical industry, has the flexibility to rapidly change the amount and type of materials produced, within wide limits, in response to raw materials shortages and market demands. This capacity and willingness to change production emphasis makes even moderate-term predictions about growth trends quite risky.

No specific information was found concerning on-site generation of steam or electricity. It is to be expected that steam, when required, will be generated on site. It is believed that electric power generally will be purchased from utility companies by contractual agreement, even for very large installations.

#### Raw Materials

Most plasticizers are products of esterification reactions between hydroxyl compounds such as alcohols or glycols and carboxylic or phosphoric acids. Commonly used catalysts are sulfuric acid and p-toluene-sulfonic acid for carboxylic acid esters and magnesium chloride for phosphoric acid esters. Appendix A contains a complete list of raw materials.

Raw materials for carboxylic acid esters are primarily aliphatic or aromatic dicarboxylic acids or anhydrides and C<sub>6</sub>-C<sub>13</sub> branched chain alcohols. The most important aromatic diacid derivatives are the phthalate esters. This group of plasticizers employs phthalic anhydride as the aromatic diacid precursor. Terephthalic acid and isophthalic acid are used to a much smaller extent. The major aliphatic dicarboxylic acid used in the production of dicarboxylic acid esters is adipic acid. Other less frequently used diacids are sebacic and azelaic acids. Mono- and tri-functional acid esters are also

produced to a small extent in the industry from mono- and tri-acids. Benzoic acid, citric acid and trimellitic anhydride are examples of acidic compounds used in the production of these less widely used plasticizers. The most important plasticizer alcohol for combination with carboxylic acids is 2-ethylhexanol (commonly referred to as octyl alcohol). Other important alcohols include isooctyl alcohol, isodecyl alcohol and butyl alcohol. In some cases mixtures of closely related alcohols rather than pure compounds are used.

Polyester plasticizers are usually of the linear variety and are made primarily from dicarboxylic acids and glycols. The acid and glycol are combined and polymerized to the required molecular weight range. Adipic acid is the most frequently used acid. Azelaic and sebacic acids are also used. The glycols vary and can be mixed.

Phosphate esters of phenolic compounds are the most important materials produced for fire-retardant plasticizers. The major acidic phosphorous compound used in the production of cyclic phosphate esters is phosphorous oxychloride,  $\text{POCl}_3$ , which is derived from phosphorous trichloride or phosphorous pentoxide and chlorine. Phenols are the hydroxyl bearing precursor. Tricresyl phosphate is produced by the reaction of  $\text{POCl}_3$  with a mixture of meta and para cresols. Mixtures of cresols and phenol will yield esters such as cresyl diphenyl phosphate. Aryl-alkyl phosphates are produced in significant quantities from mixtures of aryl-alkyl alcohols. The most important ester of this type is 2-ethylhexyl diphenyl phosphate.

Epoxidized plasticizers are prepared from natural oils (esters) such as soybean oil or linseed oil or by epoxidation of synthetic esters such as the 2-ethylhexyl ester of tall oil or oleic acids. The most widely used natural oil is soybean oil and the most important synthetic is 2-ethylhexyl tallate.

Phthalic, trimellitic and adipic acids are derived primarily from petroleum with smaller amounts of raw materials coming from coal tar. Oleic, stearic, and palmitic acids are made from animal fats. Palmitic acid is also derived from cottonseed oil. Lauric acid comes from coconut oil and ricinoleic acid from castor oil. Azelaic acid is made by ozonolysis of oleic acid. Sebacic acid is obtained by hydrolysis of castor oil. Overall, the amounts of raw materials derived from petroleum and coal greatly exceed the amounts derived from non-fossil sources.

Plasticizer alcohols can be broadly categorized as branched chain alcohols in the  $\text{C}_6$ - $\text{C}_{13}$  range and straight chain alcohols in the  $\text{C}_6$ - $\text{C}_{11}$  range. These alcohols are prepared almost exclusively from olefins derived from petroleum by the "Oxo" process, by aldol condensation, by a combination of the "Oxo" process with aldol condensation or by the use of aluminum alkyls (Ziegler catalysts). These alcohols may be prepared by reduction of fatty acid esters derived from coconut oil or tallow, but currently only small amounts of alcohols are actually prepared this way. Branched-chain alcohols or mixed isomers of branches alcohols are commonly designated by the prefix iso even though this usage does not conform to the strict chemical definition of the term. In some cases mixtures of alcohols containing 7 to 11 carbon atoms are used.

Table 3 lists several toxicological properties for a few alcohols which are used as raw materials for plasticizers.

Table 3. TOXICOLOGICAL PROPERTIES OF SOME ALCOHOLS

Alcohol	Single Oral LD50, <sup>a</sup> Rats, g/kg	Single Skin Penetration, <sup>b</sup> LD50 Rabbits ml/kg	Single Inhalation <sup>c</sup>			Primary Skin Irritation, <sup>d</sup> Rabbits	Eye Injury, Rabbits
			Vapor Concentration ppm	Time Hours	No. Killed		
1-Butanol	4.36	4.2	145 145	1 4	none of 6	none	severe
Ethanol	21.3	20 (killed one of four)	16,000	8	none of 6	minor	moderate
Ethylene glycol	8.54 <sup>f</sup>	9.53	16,000	8	none of 6	none	none
2-Ethylhexanol	7.1	2.38	16,000	8	none of 6	minor	moderate
Glycerol	27.5	>20	16,000	8	none of 6	none	none
Isobutyl alcohol	2.46	4.24	16,000	2	none of 6	none	severe
Isodecyl alcohol	9.80	3.56	16,000	8	none of 6	mild	minor
Propylene glycol	26.38	>20	8,000	8	none of 6	none	trace

FOOTNOTES:

<sup>a</sup>That quantity of undiluted chemical which kills 50% of exposed animals. Dosage is expressed as grams per kg of animal body weight.

<sup>b</sup>A 24 hour covered skin contact with the liquid chemical, or a solid in an acceptable vehicle.

<sup>c</sup>A single continuous breathing of the stated concentration of chemical in the stated period of time.

<sup>d</sup>The skin response 24 hours following application of 0.01 ml amounts to uncovered skin.

<sup>e</sup>Surface damage produced by the liquid or solid chemical or appropriate concentration thereof.

<sup>f</sup>Single dose oral toxicity to humans is greater.

Source: McClelland, C.P. Alcohols, Mono and Polyhydric. In: Encyclopedia of Polymer Science and Technology, Vol 1. H. F. Mark, ed. N.Y., Wiley, 1964.



## Products

Classes of compounds used as primary plasticizers for poly(vinyl chloride) are listed in Table 4. This list does not include mineral oils and chlorinated hydrocarbons which are usually identified as secondary plasticizers or extenders although the chlorinated hydrocarbons impart some flame resistance and flexibility.

Table 4. CLASSES OF COMPOUNDS USED AS PRIMARY PLASTICIZERS FOR POLY(VINYL CHLORIDE)

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### Monomeric esters of dicarboxylic acids or di- or polyhydric alcohols

- dialkyl adipates
- dialkyl azelates
- glycol dibenzoate esters (some)
- glycollates such as butyl phthalyl butyl glycollate
- trialkyl mellitates
- dialkyl and alkyl benzyl o-phthalates
- pentaerythritol derivatives

### Phosphoric acid esters

- triaryl phosphates
- aryl-alkyl phosphates
- trialkyl phosphates

### Polymeric plasticizers

- Polyesters of
  - adipic acid
  - azelaic acid
  - phthalic acid
- with various glycols terminated with monofunctional groups

### Epoxy compounds

- epoxidized soybean oil
- epoxidized tall oil
- epoxy resins (some)

### Miscellaneous

- phenoxy compounds
- sulfonamides

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Source: Coaker, A. W. M. and E. Musclaick. Plasticizers. In: Modern Plastics Encyclopedia, Vol 51, No. 10A. Sidney Gross, ed. N.Y., McGraw-Hill, October 1974, p. 244-252.

Different plasticizers often are chosen to impart specific properties to the finished product. Phthalic esters find substantial general purpose use in PVC film, sheeting, extrusion products, and wire and cable coatings. Adipates are used to impart low temperature flexibility to PVC formulations (e.g., vinyl meat-wrapping films). Phosphate esters are added to PVC in order to restore the fire retardancy of the unplasticized polymer when this has been diminished by addition of other plasticizers not containing a fire-retardant element (P, Cl, B). Polyesters are more resistant to extraction and migration than monomeric esters.

Although the plasticizers listed in Table 4 are used principally in formulation of poly(vinyl chloride) products, many are compatible with other polymers. Appendix B contains a complete list of commercially available plasticizers and includes information on physical properties, compatibility with various polymers, and manufacturers.

### Companies

The companies which dominate the industry are large, integrated chemical or petrochemical companies which also produce a number of other products. In several cases the companies produce the acids and/or the alcohols from which the plasticizers are made. Some manufacturers produce poly(vinyl chloride) monomer and resins as well. Thirteen companies which had approximately 93 percent of the synthetic plasticizer capacity for the United States in 1974 are listed in Table 5.

Table 5. PLASTICIZER PRODUCTION CAPACITIES 1974

Company	Gg/yr	%
Monsanto Company	225	23.0
Union Carbide Corporation*	147*	15.0
W. R. Grace & Co.	113	11.5
United States Steel Corporation	90	9.2
Eastman Kodak Company	64	6.5
Exxon Corporation	59	6.0
FMC Corporation	50	5.0
BASF Wyandotte Corporation	36	4.0
Rohm and Haas Company	41	4.0
Stauffer Chemical Company	27	2.8
Tenneco Inc.	27	2.8
Emery Industries, Inc.	18	1.8
B. F. Goodrich Company	16	1.6

\*Union Carbide ceased production of phthalate esters in 1975. This shift significantly decreased Union Carbide's total plasticizer capacity, perhaps by as much as 100 Gg/yr.

Source: Monsanto Research Corporation. Work done under Contract 68-02-1320.

Appendix C lists companies engaged in the manufacture of materials used as plasticizers. Plant locations and materials produced are included. Capacities are listed if available. Some companies engaged in the manufacture of cosmetics, pharmaceuticals or industrial specialties also manufacture plasticizers.

### Environmental Impact

The synthetic plasticizer industry produces gaseous, solid and liquid wastes. Waste water is the major environmental problem of this industry. Hydrochloric acid gas emissions, for example, are largely controlled in phosphate ester manufacture by gas scrubbers. Solid waste is a minor pollution source which results from ester purification processes. Solid wastes include spent activated carbon and insoluble sulfate salts.

A major source of waste water from esterification of carboxylic acids is the water from neutralization and washing operations and filter backwash. These types of plasticizers are normally washed and neutralized to remove traces of  $H_2SO_4$  or other acid catalyst. Waste water can contain dilute caustic, additives, sulfates (from acid catalyst) and organics such as alcohols, monoester, and small amounts of product.

The waste water from one plant which produces diethylphthalate had very high values for biological oxygen demand, chemical oxygen demand, total organic carbon, sulfate, oil, total dissolved solids and copper. Exact values are given in Process Description 1. The waste water flow rate was 0.65 liter waste water per kg product. If these values are typical of processes involving esterification of carboxylic acids, the waste water problem lies not so much in the volume of water produced as in its poor quality. The copper concentration found for this plant is high enough to interfere with biological treatment of the water.

The waste load values from the diethylphthalate plant may be compared with those from a plant producing tricresylphosphate (TCP) (see Process 2). The comparison reveals that the TCP plant had a much higher waste water flow rate (28 liters per kg product) and much lower waste loadings for biochemical oxygen demand, chemical oxygen demand, total organic carbon, cyanide, oil, copper and total dissolved solids. Sulfate loads were comparable for the two processes. Waste loads were higher for the TCP process for all other contaminants listed. Chloride loads were quite high for the TCP process. Phenol levels are of potential concern. Although not listed in the table of contaminants, permanganate is added to phosphate esters during the purification process and manganese will be found in wash waters.

The contaminants listed are for untreated waste water and many of the potential problems with such wastes can be avoided by appropriate water treatment. Plasticizer production usually occurs at a plant at which other organic chemicals are manufactured. Pollutant emissions from the plant will depend on waste management practices, segregation or combination of waste streams, composition of wastes from other organic chemical processes conducted at the site, and waste treatment facilities.

The amount of solid waste (spent activated clay or activated charcoal) is not large. However, if the solids are disposed of by landfill, materials of unknown composition may be leached and might pose a threat of local groundwater contamination.

## Bibliography

1. Anderson, Earl V. Phthalic Anhydride Makers Forsee Shortage. Chemical and Engineering News, 53(26):10-11, June 30, 1975.
2. Billmeyer, Fred W., Jr. Textbook of Polymer Science, 2nd Ed. N.Y., Wiley, 1971.
3. Chemical Technology: An Encyclopedic Treatment, Vol IV. N.Y., Harper & Row, 1973.
4. Chemical Profile, 2-Ethylhexanol. Chemical Marketing Reporter 209(12):9, March 22, 1976.
5. Coaker, A. W. M. and E. Muschick. Plasticizers. In: Modern Plastics Encyclopedia, Vol 51, 10A. Sidney Gross, ed. N.Y., McGraw-Hill, October 1974, p. 244-252.
6. Darby, J. R. and J. K. Sears. Plasticizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol 15. Anthony Standen, ed. N.Y., Wiley, 1968, p. 720-789.
7. Directory of Chemical Producers - U.S.A. Chemical Information Services, Menlo Park, California, Stanford Research Institute, 1976.
8. Fedor, Walter S. Plasticizers. The Competitive Struggle Grows Keener. Chemical and Engineering News, 13 November 1961, p. 118.
9. Hahn, A. V., The Petrochemical Industry - Market and Economics, N.Y., McGraw-Hill, 1970, p. 620.
10. Hedley, W. H., et al. Potential Pollutants from Petrochemical Processes, Final Report. Contract 68-02-0226, Task 9, MRC-DA-406. Dayton, Ohio, Monsanto Research Corp. Dayton Lab., Dec. 1973, p. 51-5, 320, 323, 326.
11. In Plasticizers Future, Few Worries About Supply. Modern Plastics 1975 (April), 44.
12. Lundeen, Allan J. Alcohols. In: Chemical and Process Technology Encyclopedia. Douglas M. Considine, ed. N.Y., McGraw-Hill, 1974, p. 56.
13. McClelland, C. P. Alcohols, Mono and Polyhydric. In: Encyclopedia of Polymer Science and Technology, Vol 1. H. F. Mark, ed. N.Y., Wiley, 1964.
14. Phthalate Effect on Health Still Not Clear. Chemical and Engineering News, 50(38):14, Sept. 18, 1972.
15. Phthalate Plasticizers--Chisso Corp. Hydrocarbon Processing, 54:174, November 1975.
16. Pratt, Christopher J. Phosphorus. In: Chemical and Process Technology Encyclopedia. Douglas M. Considine, ed. N.Y., McGraw-Hill, 1974, p. 874.

17. Reid, Emmet, Marvin L. Peterson and John W. Way. Esterification. In: Unit Processes in Organic Synthesis, 5th Ed, Philip H. Groggins, ed. N.Y., McGraw-Hill, 1958, p. 694-749.
18. Schiller, Arthur M. Acids and Derivatives, Aliphatic. In: Encyclopedia of Polymer Science and Technology, Vol. 1. H. F. Mark, ed. N.Y., Wiley, 1964.
19. Stephens, James R. Acids and Derivatives, Aromatic. In: Encyclopedia of Polymer Science and Technology, Vol 1. H. F. Mark, ed. N.Y., Wiley, 1964.
20. Sterba, Melvin J. Petrochemical Complex. In: Chemical and Process Technology Encyclopedia. Douglas M. Considine, ed. N.Y., McGraw-Hill, 1974, p. 842.
21. U. S. Tariff Commission. Synthetic Organic Chemicals United States Production and Sales, Plasticizers. 1965 TC Publication 206; 1966 TC Publication 248; 1967 Preliminary; 1968 Preliminary; 1969 Preliminary; 1970 TC Publication 479; 1971 TC Publication 614; 1972 TC Publication 681; United States International Trade Commission, Synthetic Organic Chemicals, United States Production and Sales, Plasticizers. 1973 ITC Publication 728; 1974 Preliminary.
22. Wickson, Edward J. and Herbert P. Dengler. Higher Alcohols Grow in '70's. Hydrocarbon Processing, 51:69-75, November 1972.

## INDUSTRY ANALYSIS

There are some inconsistencies in reported production data. Plasticizer production for 1974 was reported as 858 Gg by the U.S. International Trade Commission and as 745 Gg by Modern Plastics magazine. These figures contrast with a production capacity of 980 Gg/yr estimated by the Chemical Economics Handbook. Demand for plasticizers was very strong in 1974, exceeding production. Part of the gap between reported production and capacity figures can be attributed to raw materials shortages and normal plant down time.

Other factors impact reported capacity and production values for plasticizers. In many cases the distinction between plasticizers, extenders, fire retardants, etc. is not clear. Different authors may define primary plasticizers in different ways. Second, chemicals which are used primarily as plasticizers may have other uses, and some authors report only production which is to be used as plasticizers. Third, much of the equipment used to manufacture plasticizers can be used to make more than one plasticizer, or even materials with entirely different use patterns. The capacity of a given system can be expected to be different for each material produced.

The production figures used in this report represent total production of chemicals which are used mainly as primary plasticizers. Secondary plasticizers or extenders such as mineral oil or chlorinated hydrocarbons are not included.

Quantitative waste stream compositions reported in the process descriptions are the results of measurements made for processes producing one phthalate ester plasticizer and a typical phosphate ester plasticizer. These compositions are specific for the plant and product investigated and are not intended to represent raw waste loads for other processes. Specifically, diethyl phthalate (DEP), a plasticizer not used in PVC, is produced by a batch process in insignificant quantities. Since large scale production of plasticizers used in PVC such as di(2-ethylhexyl) phthalate (DOP), diisooctyl phthalate (DIOP) and diisodecyl phthalate (DIDP) generally involves continuous rather than batch processing, the waste streams resulting from the production of DOP, DIOP and DIDP can be expected to have little relationship to the data found for DEP. No information was found regarding waste stream composition associated with the production of epoxy-type plasticizers.

### Synthetic Plasticizer Processes

Esterification of dicarboxylic acids and fatty acids with monohydric alcohols and the production of polyesters by esterification/polymerization of dicarboxylic acids with glycols are chemically similar processes. They are treated by Process Description No. 1. Esterification of phosphoric acid (phosphorous oxychloride) requires special equipment and techniques because of the corrosive nature of the reactants and products and is treated in Process No. 2. Epoxidation is described in Process No. 3. Figures 1,2 and 3 are flow sheets describing their respective processes. Production of ester and epoxidized ester plasticizers is a relatively simple industrial process and the flow sheets reflect this simplicity.

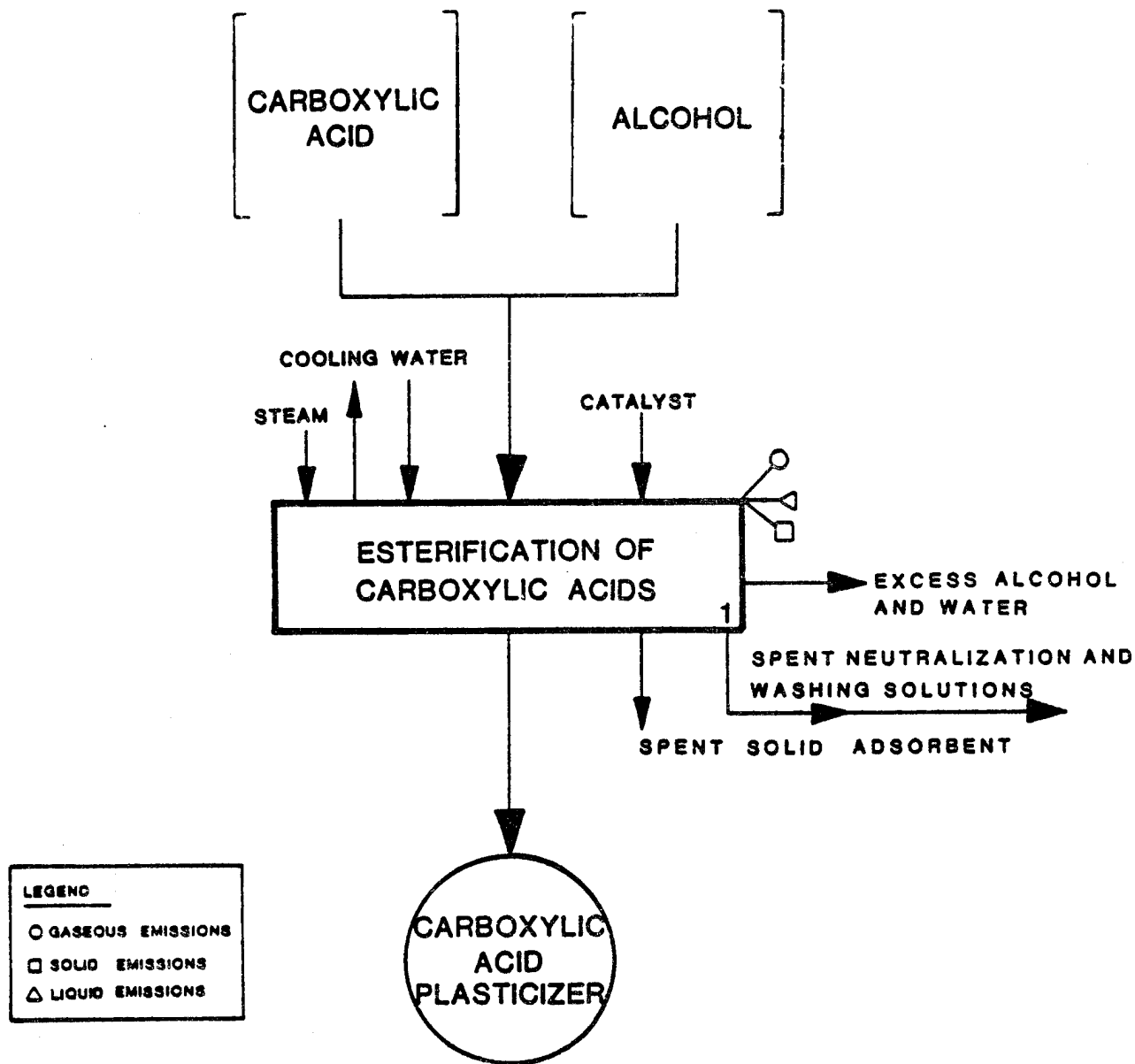


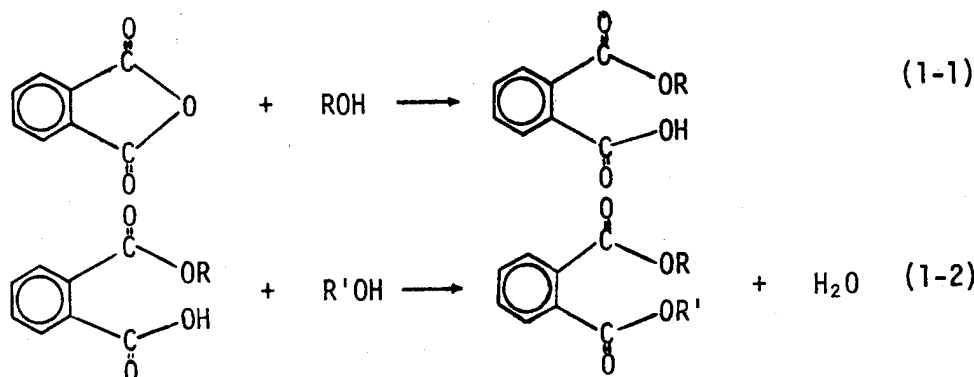
Figure 1. PROCESS FLOW SHEET FOR  
ESTERIFICATION OF CARBOXYLIC ACIDS



Esterification of Carboxylic Acids

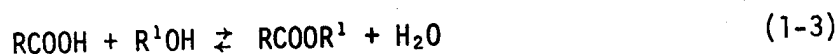
1. Function - In this process an acid or an acid anhydride combines with an alcohol to produce an ester. Most plasticizers are synthesized in simple esterification reactions, which can be carried out in the liquid phase in heated kettles with stirring and water take-off provisions. Many plants still produce plasticizers by batch methods, but newer plants operate on a continuous basis. Esterification catalysts such as sulfuric acid or p-toluene sulfonic acid are removed in a washing step. The crude product is purified by distillation, steam stripping, filtration, and treatment with activated clay or activated charcoal.

Reactions of dicarboxylic acids (or anhydrides) may be typified those of phthalic anhydride. The general reactions for their formation are shown in equations (1-1) and (1-2) where R and R' are alkyl groups.



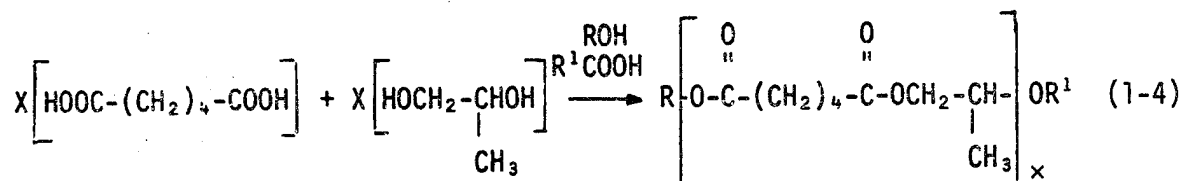
Reaction of the anhydride (1-1) proceeds under much milder conditions than does the esterification of the remaining carboxyl group (1-2). Often the anhydride is reacted with an alcohol under relatively mild conditions to produce the monoester which is then transferred to another vessel for conversion to the diester. If a diester with R and R' the same is desired, the same alcohol will be used in both reaction steps. If a mixed diester is desired, remnants of the first alcohol will be removed from the monoester before reaction of the second carboxylic acid group with a second alcohol. Usually an excess of alcohol is used and the unreacted portion recycled. Water formed by the second esterification is removed from the system to drive the reaction to completion.

The synthesis of 2-ethylhexyl tallate proceeds according to the typical esterification reaction shown in equation 1-3. The reaction may be catalyzed by sulfuric acid or hydrogen chloride:



The equilibrium reaction may be driven toward completion by several methods. With alcohols of intermediate chain length (such as 2-ethylhexanol) which are insoluble in water, stoichiometric quantities of the reactants are used and the water is removed by azeotropic distillation. With short chain alcohols, molar ratios of alcohol to fatty acid in the order of 10 or 20 to 1 are used. At such high ratios the reaction equilibrium is shifted in accordance with the law of mass action, giving yields of 95 percent or better.

Polymeric plasticizers are linear polyesters produced by the polymerization/esterification of an aliphatic dicarboxylic acid (usually adipic acid) with either pure or mixed glycols, e.g.:



R and R<sup>1</sup> are monofunctional reactants which are introduced at a suitable stage in the reaction to control the molecular weight and residual functionality. Typically, the average molecular weight of these esters is about 2000, but weights of from 800 to well over 6000 are produced for specialty applications.

2. Input Materials - The feed to the esterification unit will include an acid (or acid anhydride), an alcohol, and a catalyst. The reaction vessel may be sparged with an inert gas (CO<sub>2</sub> or N<sub>2</sub>) to suppress unwanted side reactions. In some cases an inert solvent will be added. Besides phthalic anhydride, other dibasic acids commonly used include adipic, sebacic, azelaic and fatty acids such as oleic and stearic.

Esters most commonly used as plasticizers include those produced by combining dicarboxylic acids with aliphatic alcohols containing one to thirteen carbon atoms and polyesters from the combination of dicarboxylic acids with polyhydric alcohols. The specific alcohol (or alcohols) and acid used to prepare any given ester can be determined from the name of the ester. For example, di(2-ethylhexyl) phthalate is prepared by reacting two moles of 2-ethylhexyl alcohol with each mole of phthalic acid (phthalic anhydride). One process using a "non-acidic" catalyst is reported to require 66.9 kg 2-ethylhexanol and 38.2 kg phthalic anhydride per 100 kg of di(2-ethylhexyl) phthalate (alternate terminology: dioctylphthalate, DOP) product. High efficiency is claimed for the process, so processes using other catalysts may require more input materials for the same amount of product.

3. Operating Parameters - Temperatures ranging from 35 to 180°C have been reported for esterification processes. In most cases, heat is required. Temperatures of 150-160°C have been listed for the production of di(2-ethylhexyl) phthalate. Reported pressures range from atmospheric to 170 kPa. Batch reaction times of 6 to 20 hours have been given.

Catalysts for esterification of carboxylic acids are acids (Lewis acids, species having an electron deficit in the outer shell, may be used). Sulfuric acid and toluenesulfonic acid are the catalysts most often used. Acidic cation exchange resins may be used as catalysts, particularly in large-scale continuous processes.

4. Utilities - One process for the preparation of di(2-ethylhexyl) phthalate lists a requirement of 75 kg steam per kg of product. It is not clear whether this value is representative of other processes. Electricity will be required for pumping and stirring and cooling water will be needed; no quantitative information was available in the references consulted.

5. Waste Streams - Atmospheric emissions consist primarily of fugitive emissions from processing equipment and evaporation of volatile components from liquid wastes. In general, the most volatile compounds associated with plasticizer esters prepared from carboxylic acids and alcohols are the alcohols used as raw materials. Unreacted alcohols are present in process streams and wastewater.

Wastewater comes from distillation of crude products, from condensate from steam stripping, from catalyst neutralization and crude product washing operations, and from filter backwash. Some equipment is used for the production of more than one ester. Equipment washdown which is required when changing from production of one ester to another generates wastewater. The wash water contains dilute caustic (from catalyst neutralization), sulfates (assuming sulfuric acid catalyst), unreacted alcohol, monoester, and relatively small amounts of other organic contaminants.

Table 6 lists pollutants in wastewater from a facility producing diethyl phthalate.

6. EPA Source Classification Code: None exists.

7. References -

- (1) Anon. Adipic Acid and Its Derivatives. E. I. DuPont de Nemours & Company, Wilmington, Delaware, 1957.
- (2) Environmental Protection Agency. Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Significant Organic Products Segment of the Organic Chemical Manufacturing Point Source Category. EPA-440/1-75/045, Group I Phase II. September 1975, p. 217, 273-4.
- (3) Fedor, Walter S. Plasticizers. The Competitive Struggle Grows Keener. Chemical & Engineering News, 13 November 1961, 118.
- (4) Mark, H. F. and N. G. Gaylord, eds. Encyclopedia of Polymer Science and Technology. Vol 1. N.Y., Wiley, 1964.
- (5) Phthalate Plasticizer--Chisso Corp. Hydrocarbon Processing, 54:174, November 1975.
- (6) Reid, Emmet, Marvin L. Peterson and John W. Way. Esterification. In: Unit Processes in Organic Synthesis, 5th Ed. Philip H. Groggins, ed. N.Y., McGraw-Hill, 1958, p. 694-749.
- (7) Shreve, R. N. Chemical Process Industries, 3rd E. N.Y., McGraw-Hill, 1967.

Table 6. RAW WASTE CONCENTRATIONS AND LOADS FOR FACILITY PRODUCING DIETHYL PHTHALATE<sup>a</sup>

Contaminant	Concentration <sup>b</sup> (mg/liter)	Load <sup>c</sup> (kg/1000 kg product)
BOD5	82,600	53.9
COD	127,000	82.6
TOC	51,200	33.4
Phenol	.01	.00001
NH <sub>3</sub> - Nitrogen	1.1	.00073
Total Kjeldahl Nitrogen	3.9	.00258
Cyanide	.04	.00003
Sulfate	2,030	1.33
Oil	12,500	8.17
Total Phosphorous	3.29	.00215
Zn	3.95	.00258
Cu	97.9	.0640
Fe	4.49	.00293
Total Cr	.076	.00005
Cd	.151	.0001
Total Suspended Solids	101	.0661
Total Dissolved Solids	94,800	61.9
Chloride	160	.104

<sup>a</sup> Process flow of 653 liters per 1000 kg product was reported.

<sup>b</sup> Raw waste concentrations are based on unit weight of pollutant per unit volume of process waste waters.

<sup>c</sup> Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

Source: Environmental Protection Agency, Effluent Guidelines Division. Development Document for Interim Final Effluent Limitations and New Source Performance Standards for the Significant Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA-440/1-75/045. Washington, D.C., Sept. 1975.

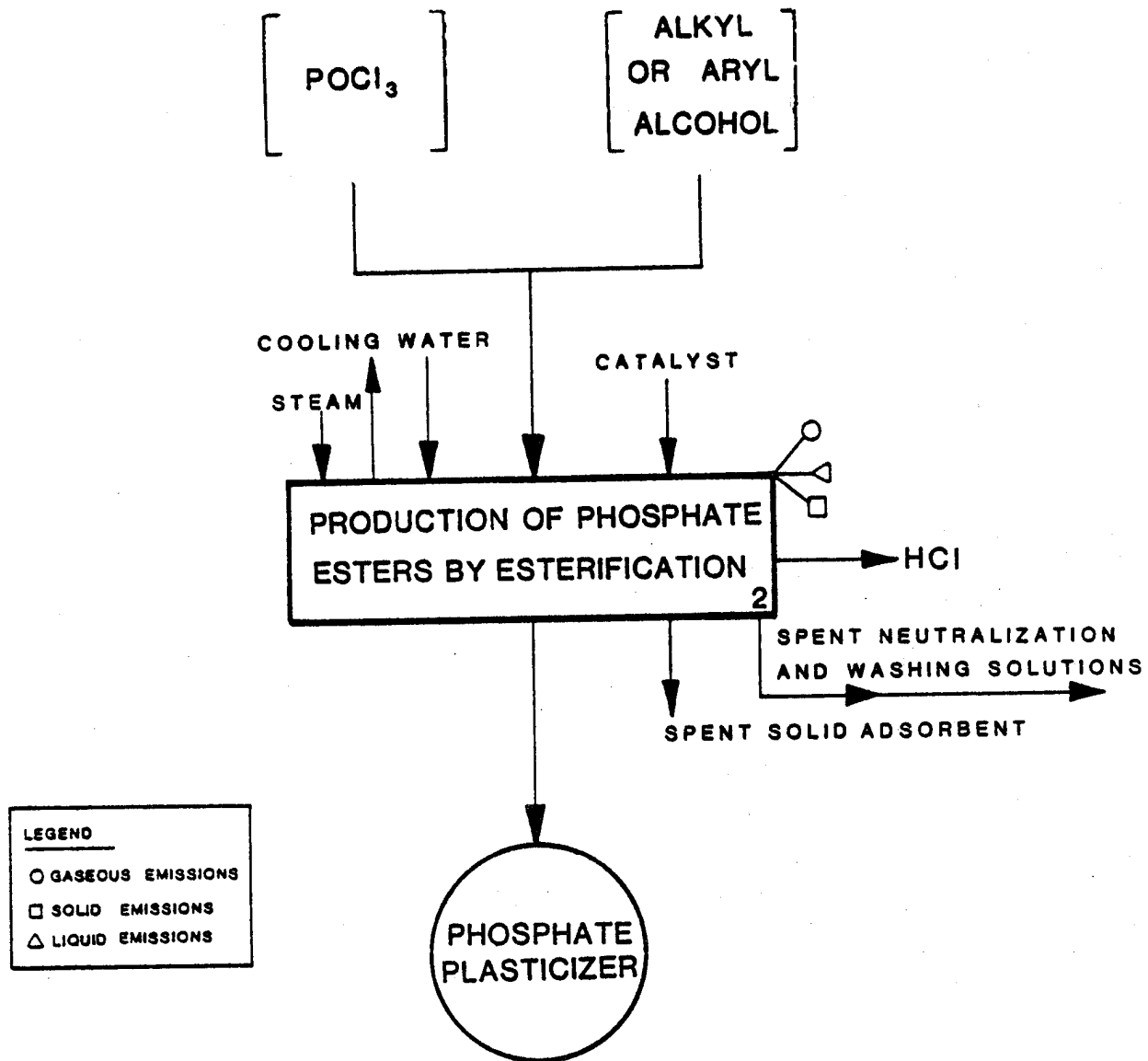
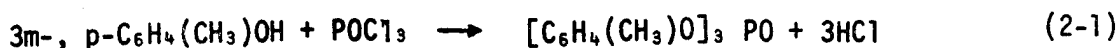


Figure 2. PROCESS FLOW SHEET  
FOR PRODUCTION OF PHOSPHATE ESTERS

Production of Phosphate Esters by Esterification

1. Function - Phosphate plasticizers are prepared by condensation of  $\text{POCl}_3$  (phosphorous oxychloride) with an alcohol or a mixture of alcohols. Cresols, phenols or xylenols are most commonly used. Mixed alkyl-aryl esters may be prepared by successive reaction with appropriate alcohols. The reaction for cresols may be written:



The production of HCl causes some processing problems. Hydrogen chloride can be removed by a current of air or neutralized by the addition of alkali. Glass-lined or alloy kettles are used because the reaction mixture is highly corrosive. The process may employ a distillation column for preliminary purification of the alcohol feed, a reactor, an ester refining column (for washing), a stripping column, and a filter. Steam ejector jets and barometric condensers may be employed for providing reduced pressures.

Although variations may exist in the sequence of operations and the amount of purification required for different applications, standard purification techniques are used. Preliminary purification typically involves direct flash distillation of the crude reaction mixture and washing with dilute caustic. The dilute caustic neutralizes residual HCl, hydrolyzes and extracts traces of partial esterification products, and extracts unreacted cresylic compounds. Addition of lime to the crude reaction mixture before distillation has been reported as a means of reducing corrosion. Final purification of plasticizer-grade products employs further washing with dilute caustic and water, steam stripping, treatment with dilute permanganate solution, dehydration by heating under reduced pressure, bleaching with activated carbon and filtration. The use of an amphoteric metal in conjunction with an alkaline wash has been reported to improve the color of the product.

2. Input Materials - The most common phosphate ester used as a plasticizer is tricresyl phosphate. Phosphorous oxychloride ( $\text{POCl}_3$ ) and a mixture of m- and p-cresols, which may contain as much as 30 to 40 percent xylenols, are input materials for plasticizer-grade tricresylphosphate. The ortho form of tricresyl phosphate is considerably more toxic than esters derived from other isomers. Therefore, the o-cresol content of the cresol feed is usually less than three percent.

3. Operating Parameters - Condensation of cresols and phosphorous oxychloride is carried out at elevated temperatures. Depending on the catalyst used, temperatures range from 150 to 300°C. A slight excess of cresol favors complete esterification. Condensation times of 6 to 9 hours at 200°C are typical when metal halide catalysts such as  $\text{MgCl}_2$  are used. Condensation may be carried out under moderate pressure to minimize loss of phosphorous oxychloride in the HCl off-gas; otherwise, each process step is carried out under reduced pressure.

4. Utilities - No information was found in the literature consulted for this study. Steam, cooling water and process heaters will be required.

5. Waste Streams - Emissions of cresols (and/or other aromatic alcohols) to the atmosphere can be expected from barometric condensers.

Waste water comes from barometric condensers, from HCl scrubbers and from preliminary and final purification steps. Caustic washing produces waste water containing dilute caustic, unreacted phenols and partial esters. Waste water from final purification contains additives washed from the product such as permanganate or permanganate reduction products. Table 7 lists pollutants from one facility producing tricresylphosphate.

The major solid waste from the production of phosphate esters is spent activated carbon from the final purification step.

6. EPA Source Classification Code - None exists.

7. References -

- (1) Billmeyer, Fred W., Jr. Textbook of Polymer Science, 2nd Ed. N. Y., Wiley, 1971.
- (2) Environmental Protection Agency, Effluent Guidelines Division. Development Document for Interim Final Effluent Limitations and New Source Performance Standards for the Significant Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA-440/1-75/045. Washington, D. C., Sept. 1975, p. 217, 273-4.
- (3) Pratt, Christopher J. PHOSPHORUS. In: Chemical and Process Technology Encyclopedia. Douglas M. Considine, ed. N.Y., McGraw-Hill, 1974, p. 874.
- (4) Reid, Emmet, Marvin L. Peterson and John W. Way. Esterification. In: Unit Processes in Organic Synthesis, 5th Ed. Philip H. Groggins, ed. N.Y., McGraw-Hill, 1958, p. 694-749.
- (5) Van Wazer, John R. Phosphoric Acid and Phosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol 15. Anthony Standen, ed. N.Y., Wiley, 1968, p. 324-6.

Table 7. RAW WASTE CONCENTRATIONS AND LOADS FOR FACILITY PRODUCING TRICRESYL PHOSPHATE <sup>a</sup>

Contaminant	Concentration <sup>b</sup> (mg/liter)	Load <sup>c</sup> kg/1000 kg product
BOD	40.	1.12
COD	408.	11.4
TOC	70.	1.96
Phenol	10.8	.304
NH <sub>3</sub> -N	3.65	.102
Total Kjeldahl N	11.8	.344
Sulfate	54.	1.513
Oil	10.5	.297
Total Phosphorous	1.19	.0335
Zn	.327	.0914
Cu	.07	.00197
Fe	1.31	.0366
Total Cr	.041	.00115
Cd	.041	.00115
Total Suspended Solids	4.	.110
Total Dissolved Solids	615.	17.2
Chloride	2,560.	71.5

<sup>a</sup>Process flow of 28 m<sup>3</sup> per 1000 kilograms product was reported. These data are for a plant using steam ejectors and barometric condensers for each process step.

<sup>b</sup>Raw waste concentrations are based on unit weight of pollutant per unit volume of process waste waters.

<sup>c</sup>Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

Source: Environmental Protection Agency, Effluent Guidelines Division. Development Document for Interim Final Effluent Limitations and New Source Performance Standards for the Significant Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA-440/1-75/045. Washington, D. C., Sept. 1975, p. 217, 273-4.



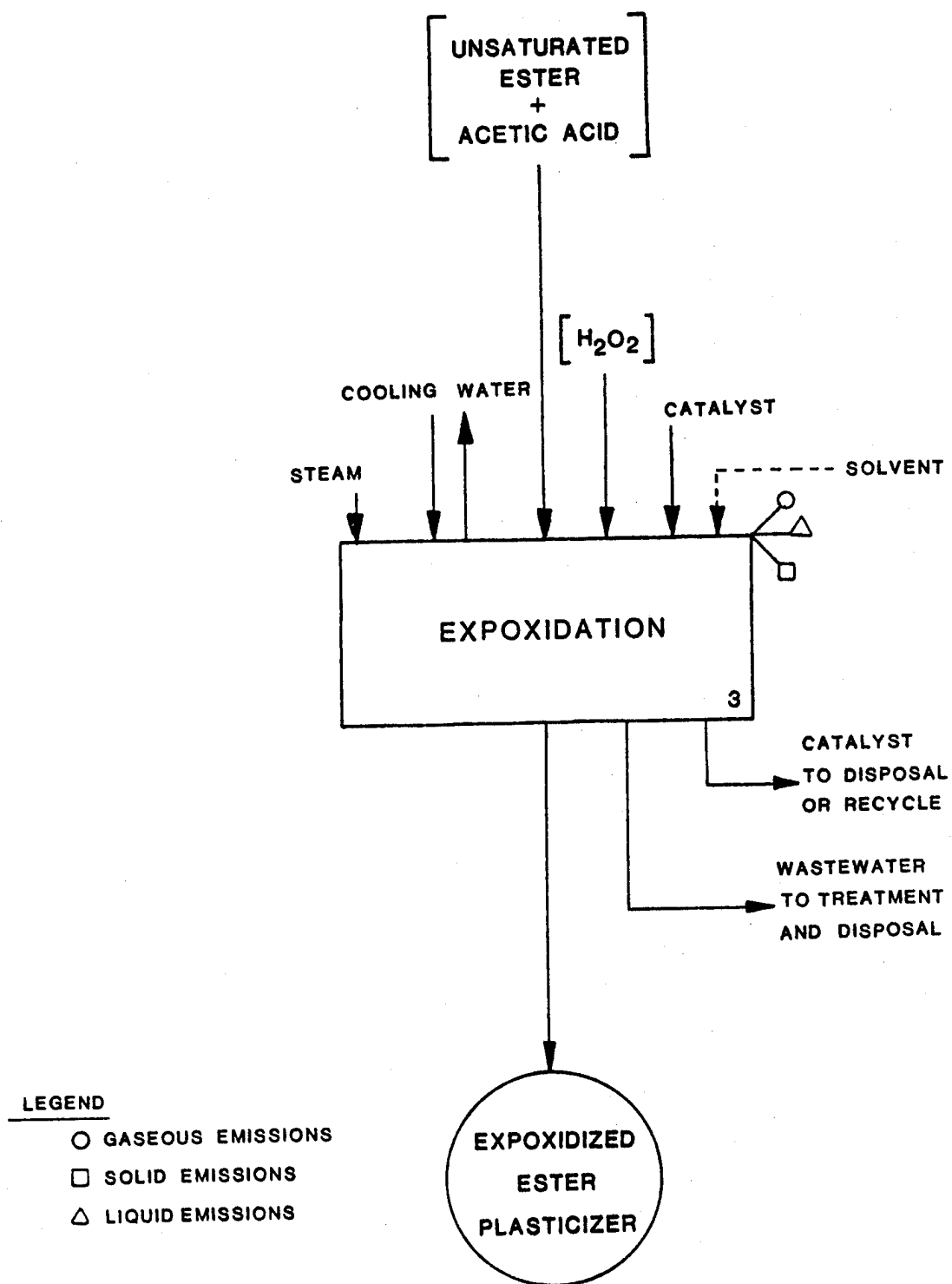
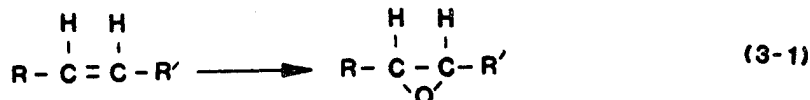


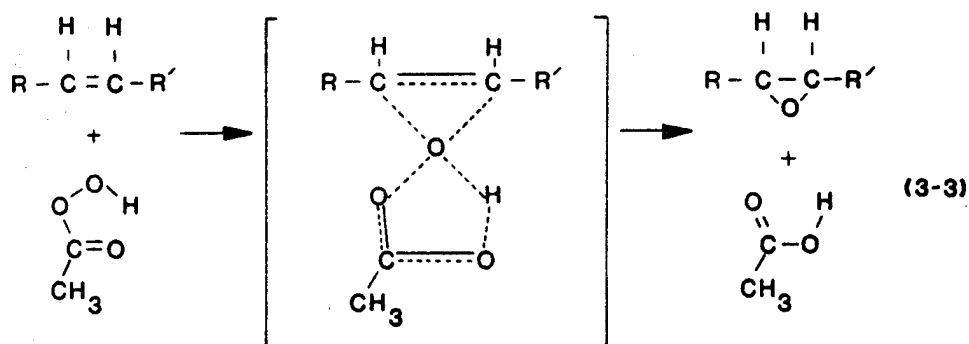
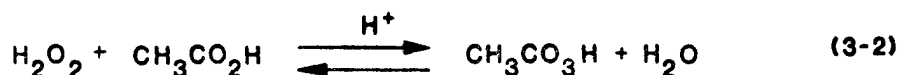
FIGURE 3. PROCESS FLOW SHEET FOR PRODUCTION OF EPOXIDIZED ESTERS

Epoxidation

1. Function - Epoxidation is defined as the reaction in which double bonds in unsaturated (olefinic) esters are converted to cyclic three-membered ethers by an active oxygen agent, as in equation 3-1.



Hydrogen peroxide is the principal oxygen source for this conversion but it must be transformed into a more active form for effective use in commercial epoxidation. Most production systems involve the preparation of peroxyacetic acid (Equation 3-2) which is then thought to interact with this double bond according to Equation 3-3.



Where possible, epoxidation reactions are carried out with peroxyacetic acid formed in situ. A one step reaction is employed in which the peroxyacetic acid is formed and used in the presence of the material to be epoxidized. The hydrogen peroxide is charged to the reaction vessel or the unsaturated ester, a catalyst, and glacial acetic acid. Reaction conditions must be controlled to minimize subsequent opening of the epoxy ring and formation of unwanted by-products.

In the widely used Archer-Daniels-Midland process, epoxy ring opening by the sulfuric acid catalyst is retarded because the system is heterogeneous, consisting of an oil phase and an aqueous phase containing the hydrogen peroxide and acetic acid. In another process based on sulfuric acid catalyses (FMC Corporation) an inert solvent such as benzene or hexane is used to reduce the effect of sulfuric acid in catalyzing epoxy ring opening. Epoxidation may be catalyzed also by the addition of poly(styrenesulfonic acid) resin.

Resin catalyzed systems are characterized by high epoxy yields, little by-product formation, nearly complete elimination of olefinic structure, low reaction temperatures and short reaction times. Because of the relative expense of the resin catalyst, conservation measures are mandatory. These involve either recycle of the resin or the use of minimal quantities of resin with corresponding increases in reaction temperature and time.

Batch production methods are used for epoxidation reactions, but considerable work on development of continuous production systems has been completed. Such methods have been found to offer promise and might be adopted if demand for epoxidized products continues to grow.

In the FMC process described above, the reaction is carried out in a stainless steel reaction vessel fitted with an agitator, cooling coils, reflux condenser, vent, rupture disc, sample line, direct and recording thermometers, feed lines and a manhole. The vessel is equipped with a system for automatically flooding the reaction with water in emergencies.

The Archer-Daniels-Midland system is apparently a two-step epoxidation process in which fresh unsaturated ester is partially epoxidized by continuous agitation with a semi-spent acid containing 1 to 2 percent sulfuric acid, 25 to 30 percent acetic acid and 5 to 6 percent unused active oxygen. The partially epoxidized ester is then separated from the aqueous (acid) phase and reacted with a fresh acid (hydrogen peroxide and acetic acid with sulfuric acid as a catalyst) to complete its epoxidation. The acid from this final epoxidation is then used to partially epoxidize fresh unsaturated ester as described above.

2. Input Materials - The unsaturated ester may be a natural oil such as soybean oil or linseed oil or it may be one of a number of synthetics such as the n-butyl or 2-ethylhexyl esters of tall oil acid or oleic acid. Peroxyacetic acid may be preformed and added in a solvent or it may be formed in situ from hydrogen peroxide and acetic acid in the presence of a catalyst and the unsaturated ester. Table 8 lists quantities of input materials for sulfuric acid catalyzed batch epoxidation of soybean oil by the FMC process.

TABLE 8. INPUT MATERIALS FOR BATCH EPOXIDATION OF SOYBEAN OIL (FMC PROCESS)

Material	Quantity	
	(kg)	(lbs)
Soybean Oil	907	2,000
Hexane	181	400
Acetic Acid (glacial)	145	320
Sulfuric Acid (50%)	361	796
Hydrogen Peroxide (50%)	347	765

Source: Wallace, John G. Epoxidation. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. Anthony Standen, ed., New York, Wiley, 1968, p. 254.

In processes using poly(styrenesulfonic acid) resin as a catalyst, almost complete epoxidation occurs when relatively large amounts of the resin are used. In a typical reaction, a quantity of fatty oil or ester containing 1.0 mole of unsaturation is mixed with 0.55 moles of glacial acetic acid and 12 percent dry resin based on the weight of epoxidizable material. Hydrogen peroxide (1.1 moles) is added slowly to facilitate control of the reaction temperature. After the reaction has reached completion the liquid is decanted or filtered, leaving the resin catalyst in the reactor for succeeding runs.

Specific data relating to reaction efficiency of the various methods for epoxidation of unsaturated esters were not found in the sources consulted for this study. A typical materials list for the epoxidation of soybean oil (iodine value of 130) using the repeated resin process is shown in Table 9.

TABLE 9. INPUT MATERIALS FOR RESIN CATALYZED EPOXIDATION OF SOYBEAN OIL

Material	Amount Used (mg/kg final product)
Soybean Oil	935
Hydrogen Peroxide (70%)	252
Acetic Acid (glacial)	95
Resin	10

Source: Wallace, John G. Epoxidation. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. Anthony Standed, ed. New York, Wiley, 1968, p. 258.

3. Operating Parameters - The FMC process for epoxidation of soybean oil employs a stainless steel reaction vessel with a capacity of 2.27 m<sup>3</sup> (600 gal). Common (18-8) stainless steel such as types 304 and 316 are satisfactory for both peroxyacetic acid formation and epoxidation reactions, with type 316 preferred. Welds in reactors and tanks are avoided as much as possible since the welds contribute to decomposition of active oxygen and may be subject to corrosion. Storage tanks for hydrogen peroxide are constructed of high-purity (99.6%) aluminum. All equipment must be thoroughly cleaned to remove any foreign materials which would decompose active oxygen. The stainless steel surfaces are passivated with nitric acid or glacial acetic acid containing small amounts of hydrogen peroxide. Continued use tends to improve the passive condition of the equipment surfaces.

Reaction times and temperatures vary according to the particular method used for epoxidation as shown in Table 10.

TABLE 10. OPERATING PARAMETERS FOR SEVERAL EPOXIDATION PROCESSES

Process Name	Catalyst	Addition Temperature	Reaction Temp.	Reaction Time	Batch Size
Archer-Daniels-Midland	Sulfuric Acid	50°-60°	50°-60°	13 hr.	N.A.
FMC	Sulfuric Acid	50°-60°	60°-65°	- <sup>a</sup>	907 kg
Repeated Resin	Poly(styrenesulfonic acid)	<60°	60°	4 hr.	N.A.
Miminal Resin	Poly(styrenesulfonic acid)	N.A.	75°-80°	7-8 hr.	N.A.

<sup>a</sup>Reaction is continued until hydrogen peroxide has been consumed.  
N.A.-indicates data is not available.

Source: Wallace, John G. Epoxidation. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. Anthony Standen, ed., New York, Wiley, 1968.

4. Utilities - No quantitative information was found on utility requirements. Electricity is required for pumping and agitation. Most process configurations require steam for initial heating and cooling water for temperature control during the reaction.

5. Waste Streams - No information was available on the amount or composition of waste streams. Fugitive emissions of acetic acid vapors can be expected. In processes using sulfuric acid catalyst, spent process water will contain high concentrations of sulfates, be saturated with epoxidized oil product and contain materials added to destroy peroxides. In processes using ion-exchange resins the spent process water will have a lower sulfate content but will contain resin degradation products. Additional waste water comes from operations which wash the product. These waters will contain the same materials as spent process liquors but in lower concentrations in most cases. Spent resin used as catalyst is a solid waste.

6. EPA Source Classification Code - None Exists.

## 7. References -

Darby, J. R. and J. K. Sears. Plasticizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol 15. Anthony Standen, ed. N.Y., Wiley, 1968, p. 720-789.

Jones, Robert W. and K. T. Chandy. Synthetic Plastics. In: Riegei's Handbook of Industrial Chemistry, 7th Ed. James A. Kent, ed. N.Y., Van Nostrand Reinhold, 1974, p. 292.

McBroom, John W. Stabilizers (PVC). In: Chemical and Process Technology Encyclopedia. Douglas M. Considine, ed. N.Y., McGraw-Hill, 1974, p. 1058.

Reents, Curtin A. Ion Exclusion. In: Chemical and Process Technology Encyclopedia. Douglas M. Considine, ed. N.Y., McGraw-Hill, 1974, p. 622.

Sheppard, C. S. Peroxides, Organic. In: Chemical and Process Technology Encyclopedia. Douglas M. Considine, ed. N.Y., McGraw-Hill, 1974, p. 838.

Wallace, John G. Epoxidation. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol 8. Anthony Standen, ed. N.Y., Wiley, 1968, p. 238-263.

APPENDIX A  
RAW MATERIALS

Table A-1. CARBOXYLIC ACIDS

---

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abietic acid  
 acetic acid (anhydride)  
 acetoystearic acid  
 acetyl citric acid  
 acetylricinoleic acid  
 adipic acid  
 azelaic acid  
  
 benzoic acid  
 butyric acid  
  
 capric acid  
 caprylic acid  
 citric acid  
  
 2-ethylbutyric acid  
 2-ethylhexoic acid  
  
 fumaric acid  
  
 hydrogenated abietic acid  
 p-hydroxybenzoic acid  
  
 isobutyric acid  
 isobutyric acid anhydride  
 isophthalic acid  
  
 lauric acid  
  
 maleic acid  
 myristic acid  
  
 oleic acid  
  
 palmitic acid  
 pelargonic acid  
 pentachlorostearic acid  
 phthalic acid (anhydride)  
  
 ricinoleic acid  
  
 sebacic acid  
 stearic acid  
 succinic acid  
  
 tall oil acids  
 tartaric acid  
 triacetoxystearic acid  
 triacetylricinoleic acid

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Table A-2. ALCOHOLS USED WITH CARBOXYLIC ACIDS

amyl alcohol	linear C <sub>7</sub> -C <sub>9</sub> alcohol
benzyl alcohol	methoxyethyl alcohol
butyl alcohol	methoxyl-ethyl alcohol
n-butyl alcohol	methyl alcohol
	methyl cyclohexyl alcohol
butoxyethoxyethyl alcohol	
butoxyethyl alcohol	neopentyl glycol
2-butoxyethyl alcohol	nonyl alcohol
	n-nonyl alcohol
capryl alcohol	
cyclohexyl alcohol	octyl alcohol
	n-octyl alcohol
decyl alcohol	
n-decyl alcohol	pentaerylthritol
diethylene glycol	phenol
diethylene glycol monoethyl ether	polyethylene glycol
dipropylene glycol	propyl alcohol
	n-propyl alcohol
ethoxyethoxyethyl alcohol	propylene glycol
ethoxyethyl alcohol	1, 2-propylene glycol
ethyl alcohol	
ethylene glycol	tetraethylene glycol
ethylene glycol monobutyl ether	tetrahydrofurfuryl alcohol
ethylene glycol monoethyl ether	tridecyl alcohol
ethylene glycol monomethyl ether	triethylene glycol
2-ethylhexyl alcohol	trimethylolethane
	2,2,4-trimethyl-1,3-pentanediol
glycerol	
	sucrose
heptyl alcohol	
n-heptyl alcohol	undecyl alcohol
hexyl alcohol	
n-hexyl alcohol	
hydroabietyl alcohol	
isobutyl alcohol	
isodecyl alcohol	
isoheptyl alcohol	
isoheptyl alcohol	
isononyl alcohol	
iso-octyl alcohol	
isopropyl alcohol	
isotridecyl alcohol	

Table A-3. ALCOHOLS USED WITH  $\text{POCl}_3$  TO MAKE PHOSPHATE ESTERS

---

butoxyethyl alcohol

butyl alcohol

chloroethyl alcohol

2-chloroethyl alcohol

cresol

dichloropropyl alcohol

dimethyl phenol

ethyl alcohol

2-ethylhexyl alcohol

isopropyl phenol

octyl alcohol

phenol

xlenol

---

APPENDIX B deleted.

## APPENDIX B

### PRODUCTS

Appendix B - Products

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APPENDIX C  
COMPANY PRODUCT LIST

Table C-1. COMPANY/PRODUCT LIST

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Akzona, Inc. Armak Co. subsid. Armak Indust. Chems. Div.	Philadelphia, PA	2-Butoxyethyl oleate 2-Butoxyethyl stearate n-Butyl oleate n-Butyl stearate Dibutyl tartrate Ethylene glycol monomethyl ether stearate Isobutyl palmitate Isobutyl stearate Isopropyl myristate Isopropyl oleate Isopropyl palmitate Isopropyl stearate Ricinoleic and acetylricinoleic acid esters (unspecified)	
Ashland Oil, Inc. Ashland Chem. Co., div. Chem. Products Div.	Mapleton, IL	n-Butyl stearate Isopropyl myristate Isopropyl palmitate Polymeric plasticizers Triethylene glycol di (caprylate-caprate)	7 <sup>+</sup>

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
BASF Wyandotte Corp. Colors and Chems. Group	Kearny, NJ	Di(2-ethylhexyl) phthalate	36 <sup>+</sup>
Borg-Warner Corp. Borg-Warner Chems. Chemicals Div.	Morgantown, WV	Triphenyl phosphate	
Chemical & Pollution Sciences, Inc.			
CPS Chem. Co. Div.	Old Bridge, NJ	Butyl cyclohexyl phthalate	
CPC International Inc. S. B. Penick & Co., div. Parsons-Plymouth Div.	Lyndhurst, NJ	Isopropyl myristate Isopropyl palmitate Isopropyl stearate	
Chemol, Inc.	Greensboro, NC	n-Butyl oleate n-Butyl stearate Glyceryl monostearate	
Cindet Chems., Inc.	Greensboro, NC	n-Butyl oleate	
Continental Oil Co. Conoco Chems. Div.	Aberdeen, MS	Phthalic anhydride esters (unspecified)	14 <sup>+</sup>

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Cyclo Chemicals Corp.	Miami, FL	Diisohexyl decyl adipate	
Diamond Shamrock Corp.			
Diamond Shamrock Chem. Co.		n-Butyl stearate	
Process Chems. Div.	Cedartown, GA	Glyceryl monoricinoleate	
		Isobutyl oleate	
		Isobutyl palmitate	
		Isobutyl stearate	
		1,2-Propylene glycol mono-ricinoleate	
		n-Butyl oleate	
	Charlotte, NC	n-Butyl stearate	
		n-Butyl stearate	
	Harrison, NJ	Glyceryl monoricinoleate	
		Isobutyl oleate	
		Isobutyl palmitate	
		Isobutyl stearate	
		1,2-Propylene glycol mono-ricinoleate	
		Di-n-butyl phthalate	
	Richmond, CA	Dibutyl sebacate	
		Di (2-ethylhexyl) glycolate	
		Di (2-ethylhexyl) phthalate	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Diamond Shamrock Corp. Diamond Shamrock Chem. Co. Process Chems. Div. (Cont.)	Richmond, CA	Di (2-ethylhexyl) sebacate Di n-octyl adipate Glyceryl monoricinoleate Iso-octyl isodecyl adipate Sebacic acid esters (un-specified)	
Dow Chem. U.S.A.	Midland, MI	Di-tert-octyldiphenyl oxide Isopropylidenediphenoxy-propanol	
Eastman Kodak Co. Eastman Chem. Products, Inc., subsid. Tennessee Eastman Co., div.	Kingsport, TN	n-butyl n-octyl phthalate Di-n-butyl phthalate Di (2-ethylhexyl) adipate Di (2-ethylhexyl) phthalate Di (2-ethylhexyl) terephthalate Diethyl phthalate Di (2-methoxyethyl) phthalate Dimethyl phthalate Polymeric plasticizers Sucrose acetate isobutyrate	64 <sup>+</sup>

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974



Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Eastman Kodak Co. Eastman Chem. Products, Inc., subsid. Tennessee Eastman Co., div. (Cont.)	Kingsport, TN	Triacetin Triethyl phosphate Tri-n-octyl trimellitate Tripropionin	
Eastman Kodak Eastman Chem. Products, Inc., subsid. Texas Eastman Co., div.	Longview, TX	224 Trimethyl pentanediol-1,3-diisobutyrate	
El Paso Natural Gas Co. El Paso Products Co., subsid.	Odessa, TX	Dimethyl adipate	
Emkay Chem. Co.	Elizabeth, NJ	Isopropyl myristate	
Emery Indust., Inc.	Cincinnati, Ohio	Bis (hydroxyethyl) azelate Bis (hydroxyethyl) dimerate n-Butyl stearate Di (2 ethylbutyl) azelate Diethylene glycol dinonanoate Di-n-hexyl azelate	18 <sup>+</sup>

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Emery Indust., Inc. (Cont.)	Cincinnati, Ohio	Diisodecyl azelate Diiso-octyl azelate Dimethyl azelate Dimethyl tridecanoate Dipropylene glycol dinonanoate Epoxidized esters (unspecified) Glyceryl mono-oleate Glyceryl trioleate Isodecylnonanoate Isopropyl isostearate Isopropyl myristate Isopropyl oleate Isopropyl palmitate Propylene glycol dinonanoate Polymeric plasticizers n-Propyl oleate Tetrahydrofurfuryl oleate Triethylene glycol dinonanoate Trimethylol propane trinonanoate	
Emery Ind. Inc., Western Operations	City of Commerce, CA	Methyl octadecadienoate	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Exxon Corp. Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, LA	Diisodecyl phthalate Diisohexyl phthalate Diisononyl phthalate Di tridecyl phthalate Triisononyl trimellitate	59 <sup>+</sup>
FMC Corp. Chem Group Indust. Chem. Div.	Nitro, WV	Cresyl diphenyl phosphate Triaryl phosphate, mixed Tri (2-butoxyethyl) phosphate Tri-p-cresyl phosphate Tri-n-butyl phosphate Triisopropylphenyl phosphate Trixylyl phosphate	29* (1975)
Givaudan Corp. Chems. Div.	Bayport, TX  Clifton, NJ	Epoxidized soya oils  Isopropyl myristate Isopropyl palmitate	9 <sup>+</sup>

\*Source: Directory of Chemical Producers, 1976

<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Glyco Chems., Inc.	Williamsport, PA	Glyceryl monoricinoleate	
The B. F. Goodrich Co. B. F. Goodrich Chem. Co., div.	Avon Lake, OH	Di (2-ethylhexyl) adipate Di (2-ethylhexyl) phthalate Diisodecyl phthalate	16 <sup>+</sup>
W. R. Grace & Co. Hatco Group Hatco Chemical Div.	Fords, NJ	n-Butyl 2-ethylhexyl phthalate n-Butyl isodecyl phthalate Di-n-butyl phthalate Di (2-ethylhexyl) adipate Di (2-ethylhexyl) phthalate Diisobutyl adipate Diisobutyl phthalate Diisodecyl adipate Diisodecyl phthalate Dimethyl adipate Dimethyl sebacate Polymeric plasticizers Tri (2-ethylhexyl) trimellitate	113 <sup>+</sup>
Guardsman Chems., Inc.	Grand Rapids, MI	Polymeric plasticizers	

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
The C. P. Hall Co.	Chicago, IL	2-Butoxyethyl oleate Butoxyethyl pelargonate n-Butyl oleate n-Butyl stearate Di (2-butoxyethyl) sebacate Di-n-butyl phthalate Dibutyl sebacate Di (2-ethylhexyl) adipate Di (2-ethylhexyl) azelate Di (2-ethylhexyl) sebacate Diisobutyl adipate Diisobutyl azelate Diisodecyl adipate Diiso-octyl adipate Diiso-octyl azelate Glycerol diacetate Glyceryl monoricinoleate Glyceryl trioleate Lauric acid esters (un-specified) Polyglycol phthalate esters Polymeric plasticizers Sebacic acid esters Triethylene glycol di (caprylate-caprate)	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Henkel Inc. Standard Chem. Products Div.	Charlotte, NC	n-Butyl stearate	
Hercules, Inc. Synthetics Dept.	Louisiana, MO	Polymeric plasticizers	5 <sup>+</sup>
E. F. Houghton & Co.	Philadelphia, PA	Glyceryl mono-oleate Glyceryl monostearate Glyceryl monotallate	
Inolex Corp. INOLEX Chem & Personal Care Div.	South San Francisco, CA	Glyceryl monostearate Glyceryl monotallate	
	Philadelphia, PA	Adipic acid esters (un-specified) 2-Butoxyethyl stearate n-Butyl oleate n-Butyl stearate Glyceryl mono-oleate Glyceryl monostearate Glyceryl trioleate Iso-octyl palmitate Isopropyl myristate	

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Inolex Corp. INOLEX Chem & Personal Care Div (Cont.)	Philadelphia, PA	Isopropyl oleate Isopropyl palmitate Isopropyl stearate Polymeric plasticizers n-Propyl oleate Tri (2-ethylhexyl) trimellitate	
International Minerals & Chem. Corp. Chem. Group Sobin Chems., Inc., Subsidi. Montrose Chem. Div.	Newark, NJ	Cresyl diphenyl phosphate Dimethyl isophthalate Tri-p-cresyl phosphate	5*
International Minerals & Chem. Corp. Chem. Group Commercial Solvents Corp., subsidi.	Terre Haute, IN	n-Butyl stearate Di-n-butyl phthalate Tri-n-butyl phosphate	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Interstab Chems. Inc.	New Brunswick, NJ	Di-n-hexyl phthalate Octylene glycol diglycolate Octyl epoxy tallate	
Kay-Fries Chems. Inc.	Stony Point, NY	Diethyl phthalate Dimethyl phthalate	
Kewanee Indust., Inc. Millmaster Onyx Corp., subsid. A. Gross and Co., div.	Newark, NJ	n-Butyl oleate n-Butyl stearate Glyceryl mono-oleate Glyceryl monostearate Glyceryl trioleate n-Propyl oleate	
Monsanto Co. Monsanto Indust. Chems. Co.	Bridgeport, NJ	n-Butyl benzyl phthalate Iso-octyl benzyl phthalate	>225 <sup>+</sup> **
	Everett, MA	Dicyclohexyl phthalate Di (2-ethylhexyl) adipate Isobutyl cyclohexyl phthalate	

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

\*\* Estimated total capacity for all locations, includes 23 Gg/yr for phosphates.



Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Monsanto Co. Monsanto Indust. Chems. Co.	St. Louis, MO	Butyl chloroacetate n-Butyl phthalyl butyl glycolate N-Cyclohexyl-p-toluene-sulfonamide Diethyl phthalate Diisobutyl phthalate Dimethyl phthalate Diphenyl phthalate Ethyl-phthalyl ethyl glycolate N-Ethyl o- and p-toluene-sulfonamide Methyl phthalyl ethyl glycolate Phenoxy plasticizers	23* (1975)
	Sauget, IL	Cresyl diphenyl phosphate Tri-p-cresyl phosphate Triphenyl phosphate	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Monsanto Co. Monsanto Indust. Chems. Co.	Texas City, TX	Di (2-ethylhexyl) phthalate Di (heptyl, nonyl, undecyl) phthalate Diundecyl phthalate	
N. L. Indust. Inc. Ind. Chems. Div.	Bayonne, NJ	Butyl acetoxystearate n-Butyl acetylricinoleate n-Butyl ricinoleate Ethylene glycol monohydroxy stearate Ethylene glycol monoricinoleate Glyceryl tri (acetylricinoleate) Glyceryl triacetate Glyceryl tri (9-epoxy-12-acetoxystearate) Methyl acetylricinoleate Methyl octadecadienoate Pentaerythritol monoricinoleate Propylene glycol monohydroxy-stearate	
National Starch and Chem. Corp. Proctor Chem. Co., subsid	Salisbury, NC	n-Butyl stearate 2-Ethylhexyl stearate	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Neville Chem. Co.	Anaheim, CA	Coumarone-indene plasticizer	
	Neville Island, PA	Coumarone-indene plasticizer	
Northwest Indust. Inc.	Chattanooga, TN	Di-ethylene glycol dibenzoate	
Velsicol Chem. Corp., subsidi.		Dipropenediol dibenzoate	
		Neopentyl glycol dibenzoate	
		Polyethylene glycol dibenzoate	
		Triethylene glycol dibenzoate	
		Tri methylolthane tribenzoate	
Occidental Petroleum Corp.			
Hooker Chem. Corp., subsidi			
RUCO subsidi.	Hicksville, NY	Di(2 ethylhexyl) adipate	9 <sup>+</sup>
		Diisodecyl adipate	
		Diisodecyl maleate	
		n-Octyl n-decyl trimellitate	
		Polymeric plasticizers	
		Triethylene glycol dica- prylate	
		Triethylene glycol di (capryl- ate-caprate)	
		Tri (2-ethylhexyl) trimellitate	
		Tri isononyl trimellitate	

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Occidental Petroleum Corp. Hooker Chem. Corp., subsid. Hooker Chems. and Plastics Corp., subsid. Electrochemical and Specialty Chems. Div.	Niagara Falls, NY	Methyl dichlorostearate Methyl pentachlorostearate	
Pfizer, Inc. Chems. Div.	Greensboro, NC	Acetyl tri (n-butyl) citrate Acetyl triethyl citrate Adipic acid esters (un-specified) Di-n-butyl phthalate Dibutyl sebacate Dicyclohexyl azelate Dicyclohexyl phthalate Di (2-ethylhexyl) adipate Di (2-ethylhexyl) azelate Di (2-ethylhexyl) phthalate Di (2-ethylhexyl) sebacate Diethyl phthalate Di-n-hexyl azelate Diisodecyl adipate Diisodecyl phthalate Diiso-octyl adipate	9 <sup>+</sup>

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Pfizer, Inc. Chems. Div. (cont.)	Greensboro, NC	Diiso-octyl isophthalate Diiso-octyl and mixed dioctyl phthalates Dimethyl isophthalate Dimethyl phthalate Dipropylene glycol dinonanoate Hexyl isodecyl phthalate Hexyl iso-octyl phthalate Iso-octyl isodecyl adipate Iso-octyl isodecyl phthalate Iso-octyl palmitate Polyethylene glycol adipate Polymeric plasticizers Tricyclohexyl citrate Triethyl citrate Tri (2-ethylhexyl) citrate Tri-n-butyl citrate Tri (2-ethylhexyl) trimellitate Triisodecyl trimellitate Triisononyl trimellitate Tri-n-octyl trimellitate Tri (n-octyl/n-decyl) trimellitate	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
PVO International, Inc.	Boonton, NJ	n-Butyl stearate Glyceryl trioleate Iso-octyl palmitate Isopropyl myristate Isopropyl palmitate Polymeric plasticizers Triethylene glycol di (caprylate-caprate)	
	Richmond, CA	Methyl octadecadienoate	
Reichhold Chems., Inc.	Carteret, NJ	n-Butyl n-decyl phthalate n-Butyl n-octyl phthalate n-Butyl ricinoleate Di [2-(2-butoxyethoxyl) ethyl] adipate Di (2-butoxyethyl) adipate Di (2-butoxyethyl) sebacate Di n-butyl fumarate Di n-butyl maleate Di n-butyl phthalate Dibutyl sebacate Di (2-ethylhexyl) adipate Di (2-ethylhexyl) azelate Di (2-ethylhexyl) phthalate Di (2-ethylhexyl) sebacate Diisobutyl adipate Diisodecyl adipate	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Reichhold Chems., Inc.(Cont)	Carteret, NJ	Diisodecyl phthalate Diiso-octyl and mixed dioctyl phthalates Diiso-octyl monoisodecyl trimellitate Di tridecyl phthalate Epoxidized soya oils Epoxidized tall oils Iso-octyl isodecyl adipate Iso-octyl isodecyl phthalate 2-Methoxyethyl acetylri-cinoleate n-octyl n-decyl adipate n-octyl n-decyl phthalate Polymeric plasticizers Triiso-octyl trimellitate	
Richardson - Merrell, Inc. J. R. Baker Chem. Co., subsid.	Phillipsburg, NJ	Di-n-butyl phthalate	
Robinson-Wagner Co., Inc.	Mamaroneck, NY	Butyl myristate n-Butyl stearate Diisopropyl adipate Isopropyl laurate Isopropyl myristate Isopropyl palmitate	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Rohm and Hass Co.	Philadelphia, PA	Adipic acid esters (un-specified) Di-n-butyl phthalate Di (2 ethylhexyl) adipate Di (2-ethylhexyl) sebacate Diisodecyl adipate Diiso-octyl adipate Di (n-octyl/decyl) adipate Epoxidized esters (un-specified) Epoxidized soya oils n-octyl n-decyl adipate Polymeric plasticizers	
Rohm and Hass Tennessee Inc. subsid.	Knoxville, TN	Di (n-octyl/decyl) adipate Di (2 ethylhexyl) adipate Epoxidized soya oils Polymeric plasticizers	
Scher Brothers, Inc.	Clifton, NJ	Diisopropyl adipate Isopropyl isostearate Isopropyl laurate Isopropyl myristate Isopropyl palmitate	

\*Source: Directory of Chemical Producers, 1976



Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
The Sherwin-Williams Co. Sherwin-Williams Chems. Div.	Chicago, IL	Di-n-butyl phthalate	
Standard Oil Co. (Indiana) Amoco Chems. Corp., subsid.	Texas City, TX	Naphthalene, alkylated	
Stauffer Chem. Co. Specialty Chem. Div.	Gallipolis Ferry, WV	Cresyl diphenyl phosphate Di (2-methoxyethyl) phthalate Tri-p-cresyl phosphate Tri (2-butoxyethyl) phosphate Tri-n-butyl phosphate Triphenyl phosphate Tris (β-chloroethyl) phosphate phate Tris (dichloropropyl) phate	16* (1975)
Su Crest Corp. Breddo Food Products Corp. subsid. Dolton Mfg. Div.	Dolton, IL	Glyceryl mono-oleate Glyceryl monostearate	
Sybron Corp. The Tanatex Chem. Co., div.	Lyndhurst, NJ	Dimethyl phthalate	

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Teknor Apex Co.	Hebronville, MA	Di (2-ethylhexyl) adipate Di (2-ethylhexyl) isophthalate Di (2 ethylhexyl) phthalate Di n-hexyl phthalate Di tridecyl phthalate Diisodecyl adipate Diisodecyl phthalate Diiso-octyl adipate Diiso-octyl and mixed dioctyl phthalates 2-Ethylhexyl isodecyl phthalate Isodecyl tridecyl phthalate Iso-octyl isodecyl phthalate n-Octyl n-decyl adipate n-Octyl n-decyl phthalate Phenoxy plasticizers Phthalic anhydride esters (unspecified) Polymeric plasticizers	27 <sup>+</sup>
Tenneco Inc. Tenneco Chems., Inc. Organics and Polymers Div.	Chestertown, MD	Di-n-butyl phthalate Epoxy plasticizers Low temperature plasticizers Maleate plasticizers	

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Tenneco Inc. Tenneco Chems., Inc. Organics and Polymers Div. (Cont.)	Chestertown, MD	Nuoplas ® plasticizers Phthalate plasticizers Polymeric plasticizers Vinyl plasticizers	
1975 Directory lists the following products as being manufactured at Chestertown, MD.:			
		Di (2-ethylhexyl) adipate Di (2-ethylhexyl) azelate Di (2-ethylhexyl) sebacate Diisodecyl adipate Diisooctyl adipate n-octyl n-decyl adipate polymeric plasticizers proprietary plasticizers	
	Fords, NJ	Tri (2-butoxyethyl) phosphate Tri-n-butyl phosphate Tri (2-ethylhexyl) phosphate	Not available

\*Source: Directory of Chemical Producers, 1976

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
Thiokol Corp. Chem. Div.	Moss Point, MS	Di [2-(2-butoxyethoxyl) ethoxyl] methane Di [2-(2-butoxyethoxyl) ethyl] adipate	
Union Carbide Corp. Chems. and Plastics Div.	Institute and South Charleston, WV	Tetraethylene glycol di (2-ethylhexanoate) Triethylene glycol di-(2-ethylbutyrate) Tri (2-ethylhexyl) phosphate	Not available
	Taft, LA	Epoxidized soya oils 2-Ethylhexyl epoxytallates	27-36 <sup>+</sup>
Union Camp Corp. Chem. Products Div. **	Dover, OH	n-Butyl oleate n-Butyl stearate Dibenzyl sebacate Di-n-butyl phthalate Dibutyl sebacate Dicapryl phthalate Di (2-ethylhexyl) sebacate Dimethyl sebacate Isopropyl myristate Isopropyl palmitate Polymeric plasticizers	

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

\*\*Essentially shut down, 1975.

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
United States Steel Corp. USS Chems., div	Neville Island, PA	n-Butyl n-octyl phthalate Di-n-butyl phthalate Dibutyl sebacate Di (2-ethylhexyl) adipate Di (2-ethylhexyl) phthalate Di (2-ethylhexyl) sebacate Di n-hexyl phthalate Diisodecyl adipate Diisodecyl phthalate Diiso-octyl adipate Diiso-octyl and mixed dioctyl phthalates Di tridecyl phthalate n-Hexyl n-octyl n-decyl adipate n-Hexyl n-octyl n-decyl phthalate n-Octyl n-decyl adipate n-Octyl n-decyl phthalate n-Octyl n-decyl trimellitate Tri (2-ethylhexyl) trimellitate Triiso-octyl trimellitate	91 <sup>+</sup>
Van Dyk & Co., Inc.	Belleville, NJ	Diisopropyl adipate	

\*Source: Directory of Chemical Producers, 1976<sup>+</sup>Source: Chemical Economics Handbook, 1974

Table C-1. COMPANY/PRODUCT LIST (Continued)

Company*	Location*	Products*	Estimated Capacity (Gg/yr)
White Chem. Corp.	Bayonne, NJ	Dimethyl adipate Dimethyl sebacate	
Witco Chem. Corp. Argus Chem. Corp., subsid Halby Div.	New Castle, DE	Epoxidized linseed oil	
Witco Chem. Corp. Argus Chem. Corp., subsid	Taft, LA	Epoxidized soya oils n-Octyl epoxy stearate Octyl epoxy tallate	14 <sup>+</sup>

\*Source: Directory of Chemical Producers, 1976

<sup>+</sup>Source: Chemical Economics Handbook, 1974